Efficient blue–green light emitting poly(1,4-phenylene vinylene) copolymers†

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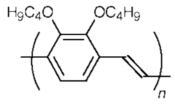
Received (in Cambridge, UK) 29th November 1999, Accepted 18th January 2000

2,3-Dialkoxy-substituted poly(1,4-phenylene vinylene) (PPV) homo- and co-polymers have been prepared by the Gilch dehydrohalogenation polycondensation of the corresponding bishalomethyl-substituted benzene monomers, and double layer light emitting devices fabricated with these materials exhibited high electroluminescence efficiencies with low turn-on voltages.

Semiconducting organic polymers exhibiting electroluminescence (EL) have recently attracted considerable interest owing to their high potential for application as the active layer in polymer light-emitting devices (PLEDs).[1–5] The 2,3-disubstituted derivatives of PPV are of interest owing to the potential distortion of the intra- and inter-molecular chain interactions as a result of steric effects.[6] Poly(2,3-dibutoxy-1,4-phenylene vinylene)[7] **1** exhibits a blue–green solid state photoluminescence (PL) with 40% efficiency which is considerably higher than the prototypical 2,5-dialkoxy-substituted analogue, MEH-PPV.[8] We have also reported a new class of 2-silylated and 2,5-disilylated PPV derivatives which essentially behave as organic solvent processible analogues of PPV itself, but which are much more luminescent (PL efficiency 60%). However, single layer (100 nm) devices fabricated from poly(2-dimethyloctylsilyl-1,4-phenylene vinylene) (DMOS-PPV)[9,10] **2** and poly[2,5-bis(dimethyloctylsilyl)-1,4-phenylene vinylene] (BDMOS-PPV)[11] **3** suffered from rather high turn-on voltages of *ca.* 15 V. It has recently been reported that high efficiencies may be realised in ternary statistical copolymers of PPV derivatives,[12] and that the degree of defects is determined in part by non-regioregular coupling of the putative quinomethide precursor in the Gilch polycondensation.[13]



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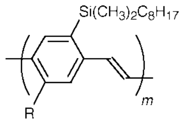
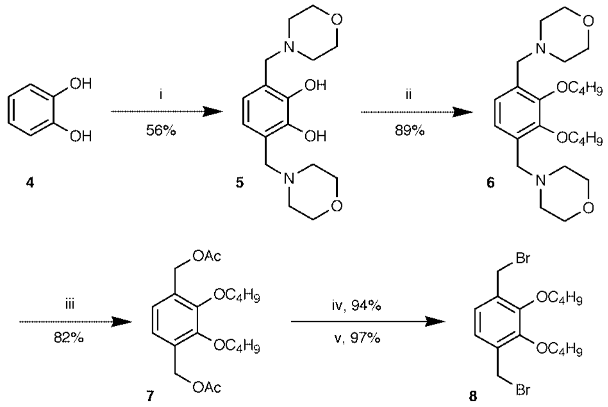


2; R = H

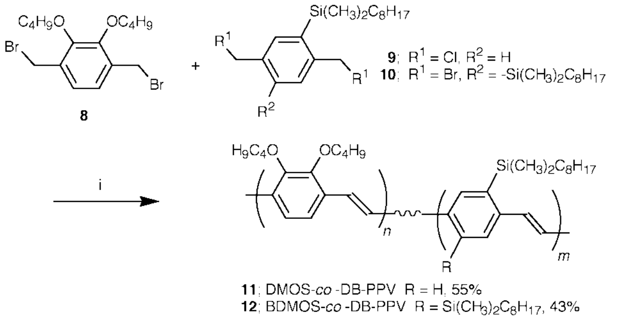
3; R = Si(CH$_3$)$_2$C$_8$H$_{17}$

Here, we report an improved synthesis of 1,4-bis(bromomethyl)-2,3-dibutoxybenzene **8** and the exploitation of two important monomers to yield the statistical copolymers poly[(2-dimethyloctylsilyl-1,4-phenylene vinylene)-*co*-(2,3-dibutoxy-1,4-phenylene vinylene)] (DMOS-*co*-DB-PPV) **11** and poly-{bis[(2,5-dimethyloctylsilyl)-1,4-phenylene vinylene]-*co*-(2,3-dibutoxy-1,4-phenylene vinylene)} (BDMOS-*co*-DB-PPV) **12**, respectively, that combine the intrinsically high electroluminescence present in the three corresponding homopolymers **1**–**3** with the significantly reduced turn-on voltages of 2,3-dialkoxy-substituted PPVs.

The synthesis of the 2,3-dibutoxy monomer **8** is shown in Scheme 1. The key improvements were the use of the double Mannich reaction to introduce both carbon substituents and the conversion of the diol formed from saponification of the diacetate **7** with CBr$_4$ and PPh$_3$[14] into the crystalline 1,4-bis-bromomethyl compound **8**.‡ Statistical copolymersation under Gilch conditions of monomer **8** with **9**[9,10] and **10**,[11] using in both cases a feed ratio of 1 : 1, in the presence of excess KOBu^t in degassed THF at room temperature (Scheme 2) gave the copolymers **11** and **12**, respectively. The polymers were purified by precipitation from methanol and acetone or mixtures of methanol–water, respectively, and formed bright yellow fibres displaying high luminescence. ^{1}H NMR side-chain analysis of DMOS-*co*-DB-PPV **11** gave the ratio *n* : *m* of 3 : 4 and for BDMOS-*co*-DB-PPV **12** of 4 : 3.



Scheme 1 *Reagents and conditions*: i, CH$_2$O, morpholine, Pr^{i}OH, reflux, 1 h. ii, C$_4$H$_9$Br, K$_2$CO$_3$, EtOH, reflux, 20 h. iii, Ac$_2$O, NaOAc, HOAc, reflux, 72 h. iv, K$_2$CO$_3$, MeOH–THF–H$_2$O (50 : 9 : 3), 48 h. v, CBr$_4$, PPh$_3$, THF, 4 h.



Scheme 2 *Reagents and conditions:* i,KOBu^t, THF, 18 h.

Molecular weight determination of the purified polymers using size-exclusion chromatography (SEC) calibrated with polystyrene standards and multiple angle light scattering revealed high molecular weights and polydispersities, typical of dehydrohalogenation polycondensations (DMOS-*co*-DB-PPV: M_n = 290 000, M_w/M_n = 7.1; BDMOS-*co*-DB-PPV: M_n = 180 000, M_w/M_n = 5.5). DMOS-*co*-DB-PPV **11** and BDMOS-

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† Electronic supplementary information (ESI) available: normal optical absorption, PL and EL spectra (Fig. S1) and cyclic voltammograms (Fig. S2) for BDMOS-DB-PPV. See http://www.rsc.org/suppdata/cc/a9/a909382f/

co-DB-PPV **12** readily dissolved in aprotic solvents such as THF, chloroform or xylene and formed good uniform transparent films on ITO-coated glass substrates. The thermal properties of the polymers were investigated by thermal gravimetry (TG) and differential scanning calorimetry (DSC) under nitrogen. Analysis of the TG trace (heating rate 10 °C min^{-1}) for DMOS-*co*-DB-PPV and BDMOS-*co*-DB-PPV revealed a 5% weight loss at *ca*. 370 and 320 °C, respectively. BDMOS-*co*-DB-PPV showed an exothermic phase transition at *ca*. 170 °C.

Optical absorption measurements in $CHCl_3$ solutions for DMOS-*co*-DB-PPV and BDMOS-*co*-DB-PPV showed λ_{max} of 440 and 442 nm, respectively. Interestingly, DMOS-*co*-DB-PPV showed for the λ_{max} in the solid-state a bathochromic shift to 448 nm, whereas BDMOS-*co*-DB-PPV revealed a slightly hypsochromically shifted value of 440 nm (Fig. S1 in ESI). The longest wavelength absorption maxima reflected the statistical composition of the respective monomeric building blocks; DB-PPV **1**: λ_{max} = 454 nm; DMOS-PPV **2**: λ_{max} = 414 nm; BDMOS-PPV **3**: λ_{max} = 436 nm. Both polymers are bright yellow materials exhibiting high solid-state PL efficiencies of 35 and 28%, with the longest wavelength emission peaks at λ_{em} = 548 nm (2.26 eV) and λ_{em} = 544 nm (2.28 eV, (Fig. S1 in ESI)), respectively.

Cyclic voltammetry (CV) was perfomed on thin polymer films of BDMOS-*co*-DB-PPV **12** spin-coated onto Pt disk electrodes in MeCN using a Pt wire as counter electrode and Ag/AgCl as a reference. In the anodic scan the onset of oxidation occurred at *ca.* 1.2 V followed by three subsequent non-reversible oxidations at 1.38, 1.63 and 1.80 V, respectively (Fig. S2 in ESI). The cathodic sweep showed onset of reduction at *ca.* −1.6 V and a quasi-reversible reduction step at −1.83 V (Fig. S2 in ESI). The electrochemically measured band gap was 2.8 V, which compares well with the HOMO–LUMO energy gap of 2.82 eV as measured from UV–VIS spectroscopy. The HOMO and LUMO energy levels of BDMOS-*co*-DB-PPV were estimated from the oxidation and reduction onset potentials to be HOMO = 5.6 eV and LUMO = 2.8 eV, respectively.[15]

Double layer devices with the configuration ITO/PEDOT:PSS/polymer/cathode were fabricated, [PEDOT:PSS is poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)].§ Both polymers exhibited blue–green light emission. Interestingly, DMOS-*co*-DB-PPV LEDs only showed EL emission for Ca cathodes evaporated at pressures of *ca*. 10^{-3} mbar, but little or no EL for evaporation at pressures $\leqslant 3 \times 10^{-6}$ mbar. DMOS-*co*-DB-PPV **11** double layer LEDs with Al cathodes showed turn-on voltages of 2.0–2.4 V (threshold = 0.01 cd m^{-2}) with a power efficiency of 0.05 cd A^{-1} and a maximum luminance of 36 cd m^{-2} at 11 V. Substantially better performance (both efficiency and luminance) was noted for devices made with BDMOS-*co*-DB-PPV **12** and Ca cathodes compared with devices made with DMOS-*co*-DB-PPV **11**. The power efficiency was up to 0.72 cd A^{-1} with a maximum luminance of 1384 cd m^{-2} at 12 V and turn-on voltages of 4.0 V for a structure with an 80 nm active layer (Fig. 1). This compares well with a 6 V turn-on voltage for the BDMOS-PPV **3** based homopolymer device.[11] The EL emission peak was measured at λ_{em} = 533 nm (2.33 eV).

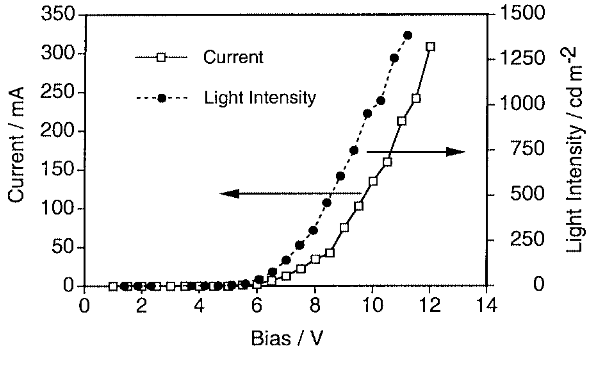

Fig. 1 Current–voltage–luminance (I–V–L) characteristics of an ITO/PEDOT (80 nm)/BDMOS-DB-PPV (80 nm)/Ca LED. The active area of the device is *ca.* 0.045 cm^2. EL emission turns on at 4.0 V and the maximum efficiency is 0.72 cd A^{-1}.

In summary, a new and versatile synthetic route for the preparation of 2,3-dialkoxy-1,4-bis(bromomethyl) monomers was developed. Improved EL performance of devices using statistical copolymers such as BDMOS-*co*-DB-PPV **12** as the active layer in comparison with the homopolymers was demonstrated, making this material a promising candidate for further optimisation.

We thank EPSRC for financial support and provision of the Swansea Mass Spectrometry Service, the Swiss National Science Foundation and Churchill College, Cambridge (Fellowships to R. E. M.), the Royal Society (University Research Fellowship to F. C.), the Commission of the European Union (Marie Curie Fellowship to F. G., TMR network 'SELOA' and Brite-Euram Contract BRPR-CT97-0469 'OSCA'), the Cambridge Commonwealth Trust and the CVCP (ORS studentship to B. S. C.) and Cambridge Display Technology (CDT) for generous support.

Notes and references

‡ All new monomers were characterised fully by their melting points, IR, ^1H and ^{13}C NMR spectroscopy, EI or CI MS spectrometry and elemental analysis.

§ Absorption and PL spectroscopy were carried out on thin films deposited onto spectrosil substrates by means of a Hewlett Packard B453 UV–VIS spectrophotometer (absorption) and of a CCD UV-enhanced spectrograph (PL). The PL efficiency was determined on films deposited on spectrosil substrates, using a nitrogen purged integrating sphere. Excitation was by means of the visible or multiline UV lines (*ca.* 351, 364 nm) of an Ar-ion laser. LEDs were prepared on commercial ITO substrates (Asahi), treated prior to use with a oxygen plasma for 10 min.[16] The PEDOT:PSS (Bayer) was coated from a water dispersion yielding a *ca.* 80 nm thick layer after drying (*ca.* 90 °C; 1 h).[17] Active layers were spin-coated from THF–*p*-xylene solutions on either the bare ITO or on ITO/PEDOT substrates to give film thickness of 80–100 nm. Cathodes (Al or Ca/Al) thermal evaporation (at *ca.* 5×10^{-6} mbar or less) completed the preparation of the diodes which were then tested in a 10^{-2} mbar vacuum.

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Communication a909382f